U.S. Army Research, Development and Engineering Command



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#### The Detonation Properties of Combined Effects Explosives

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#### Overview



- Mechanisms of metal reaction in detonation zone
- History and definition of "combined effects"
- How and why move away from Aluminum?
- Resolution of confounding factors involved in the reaction of aluminum
- Effects of early reaction on blast
- Conclusions and future work



### Al reactions in the detonation

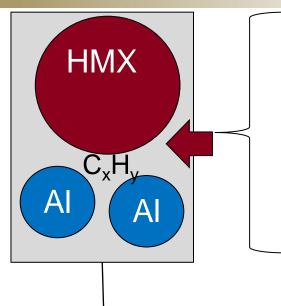


- M. Finger (*International Detonation Symposium*, 1970, 137-152, Portland, OR.) saw little Al combustion despite high oxygen balances
- F. Volk (10th International Detonation Symposium, July 12 16, 1993, Boston, MA) saw evidence of Al combustion in inert atmospheres when GAP (energetic) binders were used, but no Al combustion when all inert binders were used
- M.N. Makhov (Combustion, Explosion, and Shock Waves, 40(4), 458-466, 2004) only saw evidence of Al combustion in binder-free composites of Al and nitramine
- W. Balas (*IMEM Symposium*, Tuscon, AZ, May 12, 2009) showed evidence of early AI combustion via cylinder expansion. E. Baker and coworkers developed theory to explain Eigenvalue detonation (*12th International Detonation Symposium*, Arlington, VA, 2003, p. 195
- A. Davis (*Proceedings of the 36th North American Thermal Analysis Society Conference*, Atlanta, GA, August 17 20, 2008) showed evidence of little or no Al combustion in HTPB compositions PBXN-113 and PBXW-114.



# Reactions in the detonation (a simplified picture)



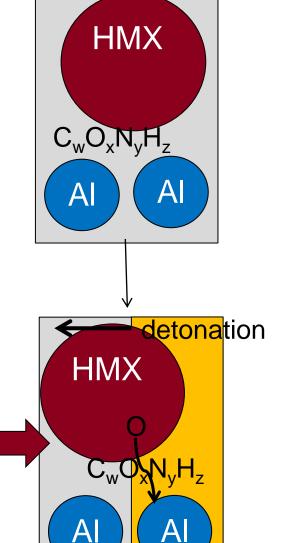


#### Non-Energetic binder

- Al particles in carbon rich binder
- Diffusion/reaction of oxygen with Al hindered by carbon rich matrix
- > 11 V/V<sub>0</sub> Al reaction delays

#### Energetic binder

- Closer proximity of oxygen to Al particles
- Diffusion/reaction of oxygen with AI not hindered by carbon rich matrix





detonation

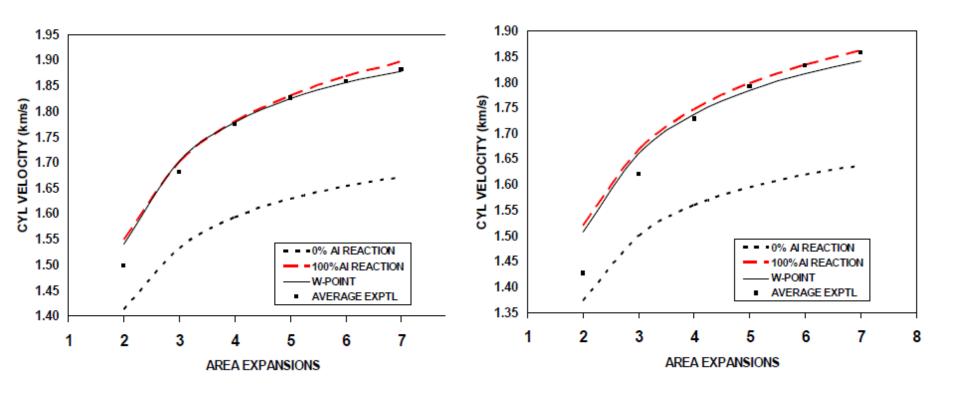
 $C_xH_v$ 

**HMX** 



# Al reactions – wall velocities of PAX-30/42



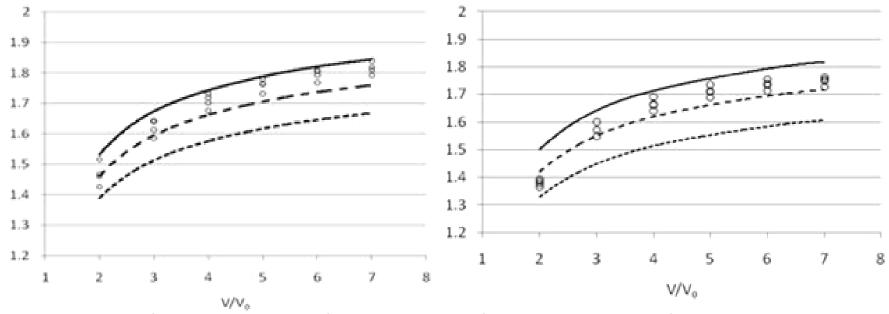


In a 1.00" (2.54cm) diameter copper cylinder expansion test, PAX-30 (left) shows equivalent Gurney constants to LX-14 using nearly all aluminum particle sizes. Al also reacts fully in RDX-based PAX-42 (right).



### Silicon reactions – wall velocities of PAX-49/50





- PAX-49 (HMX-based, left) and PAX-50 (RDX-based, right) 1-inch cylinder expansion shots show wall velocity >N-9 and ~=LX-14 with low nitramine loading (<80% by weight).</li>
- Both HMX and RDX-based explosives show nearly all silicon reacts to SiO<sub>2</sub> by 7 volume expansions.

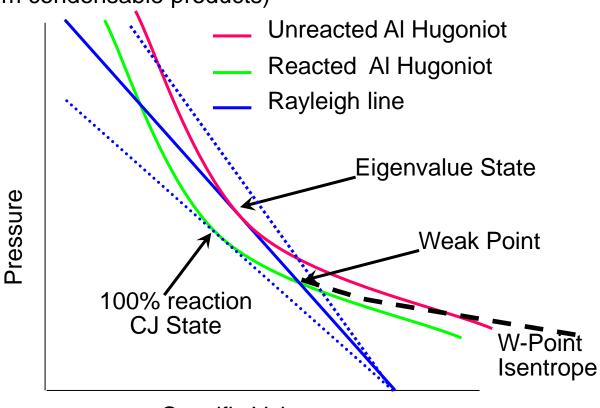
See Paula Cook's presentation for more details!



#### **Detonation phenomenon**



- Eigenvalue detonation theory is observed for aluminized combined effects explosives; CJ state for reacted Al products is displaced by amount of Al reacted
- Decreased detonation velocity (low P-v Rayleigh line slope due to decreased pressures from condensable products)

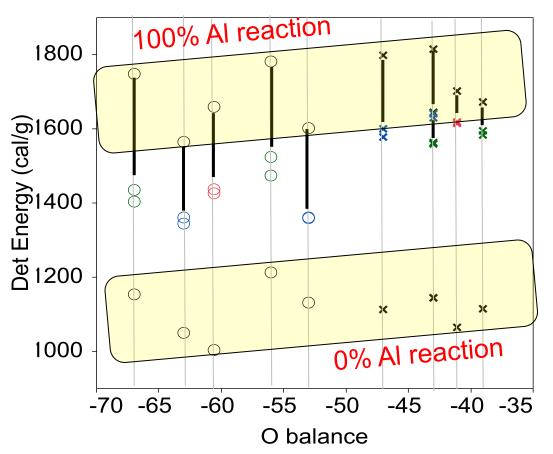




#### Why does this occur?



#### Detonation calorimetry energies in Argon



Inert binders resulted in less AI reaction, particularly with large AI size.

Energetic binder yielded reactions of Al even at different sizes but similar oxygen balances.

Data is similar when plotted as kJ/cc.

- x Energetic binder, large Al X Energetic binder, small Al
- Inert binder, large Al Inert binder, small Al,
- ♦ O 100% Al reaction (theory), x 0% Al reaction (theory)



### Revisiting the CHNO Decomposition Scheme

#### Traditional reaction scheme is

- 1. All nitrogen goes to N<sub>2</sub>
- 2. All H goes to H<sub>2</sub>O
- 3. Any O left goes to CO
- Any O left takes CO → CO₂
- 5. Any excess C goes to C(s).
- 6. M goes to  $M_xO_y$
- 2-4 are known to be dependent on sample density and confinement.<sup>1</sup>
- Since combined effects formulations show evidence that Si and Al react by 7 volume expansions, we must revisit this reaction scheme.
- 1. Kamlet and Jacobs, "Chemistry of Detonations I: Simple method for calculating detonation properties of CHNO Explosives." *J. Chem. Physics*, **28**, 1968, 23-35.

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### Revisiting the CHNO Decomposition Scheme

Mol/kg Cheetah 5.0 products, ~7 V/V0, exp6.3 library.

Gas (mol/kg):	СО	CO <sub>2</sub>	H <sub>2</sub> 0	H <sub>2</sub>	CH₄	N <sub>2</sub>
PAX-30	10.7	0.83	2.34	7.18	1.38	10.6
PAX-30 (Al inert)	3.96	6.36	6.32	0.54	2.30	10.5
PAX-50	10.4	0.42	1.17	6.91	2.09	10.6

$$\begin{array}{lll} 2 \text{ CO} \leftrightarrow \text{CO}_2 + \text{C} & -41.2 \text{ kcal/mole} \\ \text{H}_2 + \text{CO} \leftrightarrow \text{H}_2\text{O} + \text{C} & -31.4 \text{ kcal/mole} \\ \textit{High pressures} & \textit{eq} \rightarrow \\ \textit{High temperatures} & \textit{eq} \leftarrow \end{array}$$

Explosive	CO <sub>2</sub> /CO	H <sub>2</sub> O/H <sub>2</sub>	
PAX-30	0.078	0.33	
PAX-30 Al inert	1.61	11.7	
PAX-50	0.04	0.17	



## How early Al reactions effect blast



Notional	Early reaction (Anearobic O)	Late reaction (atmospheric O <sub>2</sub> ) kJ/kg explosive				Sum, kJ/kg
formulation	dH from Al rxn	dH from CO	dH from H <sub>2</sub>	dH from CH₄	dH from Al rxn	1.071.9
PAX-30 (Al early reaction)	4659	3042	4777	1107		13585
PAX-30 (Al late reaction, "blast from Al")	0	1120	130	1845	4659 (late)	7754

Time —

Two time regimes of Al reaction:

- -Early reaction of Al
- -Late reaction of AI, representing most "blast" type reactions



#### **Combined Effects**



Proper formulation of finely divided metals and semi-metals results in early metal oxidation, high Gurney energy, and higher enthalpy species (CO, H<sub>2</sub>, etc) for later blast augmentation. 30mm STAR warhead detonation sequence shown below.

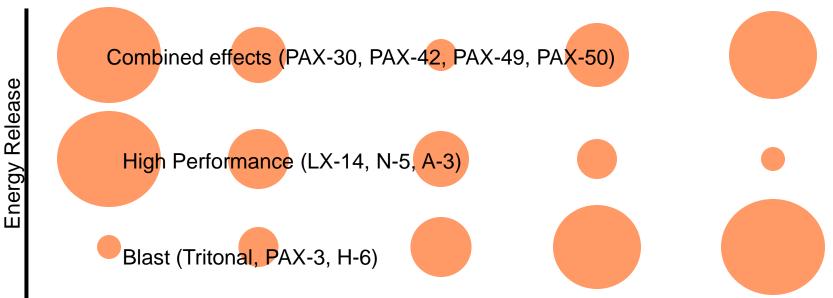














#### **Conclusions**



- Al does not react fully in non-energetic binder compositions, even at low binder content.
- Oxygen balance is not the only factor in early Al reaction since the amount of metal consumed is not linear with oxygen content, despite different binders having the same oxygen balance.
- Early reaction of metals leads to augmentation of CO/H<sub>2</sub>/CH<sub>4</sub>.
- Equivalent Al oxidation thermal energy thermal energy obtained from oxidation of CO/H₂/CH₄ is obtained.
- Silicon is a viable alternative to aluminum.